Carbon Nanotube Reinforced Poly(Trimethylene Terephthalate) Nanocomposites: Viscoelastic Properties and Chain Confinement

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ABSTRACT

Through a very facile route, a new class of nanocomposites involving poly(trimethylene terephthalate; PTT) and multiwalled carbon nanotubes (MWCNTs) was developed which was found to be high performance engineering material showing high modulus. Morphological, mechanical, viscoelastic, and thermal properties of the PTT nanocomposites with varying compositions of MWCNT were systematically studied and the results were analyzed. The dynamic mechanical and tensile properties of all the nanocomposites were seen to be enhanced with the addition of MWCNT and the sample containing 2 wt% MWCNT showing a storage modulus as much as 9.4 × 108 GPa. The results were correlated with the morphological features obtained from scanning electron microscopy and transmission electron microscopy. Coefficient of effectiveness, degree of entanglement density, and reinforcement efficiency factor were estimated from the storage modulus values and, in addition, the degree of chain confinement also could be quantified. Furthermore, theoretical modeling was also done on the elastic properties of the composites. The crystallization temperature, glass transition temperature, and percentage crystallinity were estimated for all the nanocomposites and it was found that the sample with 3 wt% MWCNT content exhibited the highest glass transition temperature of 68.2_C.

INTRODUCTION

Polymeric materials reinforced by nanofillers are of special interest in nanotechnology owing to their versatile properties and innumerable applications. The incorporation of nanofillers into the polymers can tune and modify several physical characteristics of the nanocomposites including the strength and modulus of the polymer matrix and can also enhance the thermal and thermooxidative thermooxidative degradation of the polymers [1–3]. The thermal behavior of nanocomposites can be correlated to the glass transition temperature, Tg. Among the nanocomposites, the carbon nanotube (CNTs)-based nanocomposites are known to exhibit good electrical, mechanical, and thermal properties [4,5]. The electrical conductivity shown by the

multiwalled carbon nanotubes (MWCNT) is comparable to that of copper (500–10,000 S/cm) and, in addition, the tensile strength (_20 GPa) and modulus (in the order of 1 TPa) are still higher [6]. Highly favorable conductivity of MWCNT (100–1,000 W/mK), very high aspect ratio, and good physical properties of CNT are some of the factors which have made the material a very promising and attractive candidate for composite preparations [7]. The conductivity of CNT-based polymer nanocomposite is seen to be dependent on several factors including the concentration of fillers, their aspect ratio, and degree of dispersion. Paszkiewicz et al. [8] nvestigated the effect of hybrid fillers like single-walled carbon nanotubes (SWCNT) and graphene nanoplatelets (GNP) on PTT-block-poly (tetramethylene oxide) (PTT-PTMO) and reported that the synergic effect of SWCNT and GNP enhances the thermal conductivity of PTTPTMO significantly. Kumar et al. [9] reported that at a total loading of 0.5 wt% the hybridizing effect of GNP with commercially functionalized MWCNT in polyetherimide (PEI) matrix improve the electrical and thermal conductivity, as well as the dynamic properties considerably. Logakis et al. [10] investigated the thermal, electrical, mechanical, and dielectric properties of poly(methyl methacrylate) (PMMA)/CNT nanocomposites and reported that the electrical percolation threshold was found to be at 0.5 vol%.

PTT which is an aromatic semicrystalline polyester was first synthesized by Whinfield and Dicksen in 1941 (British patent 578 079). Because of the presence of three methylene groups PTT shows good elastic recovery greater than that of other polyesters like poly (butylene terephthalate) (PBT) and poly (ethylene terephthalate) (PET) and it is comparable to that of nylon. PTT also shows good color fastness, uniform dye uptake, stain resistance, and so forth [11]. The properties of PTT are in between that of PBT and PET and hence it can be considered as a promising material for the applications such as fibers, films, and engineering thermoplastics [12]. However, PTT has some limitations like low impact strength, low heat distortion temperature, low vis-cosity for processing, and so forth [13].

Structural, mechanical, and viscoelastic properties of materials are of great importance for diverse applications and therefore a thorough characterization of these properties including stiffness and viscoelastic properties are routinely studied using dynamic mechanical analysis (DMA) technique [6]. Extensive research reports are available in the field of nanofiller reinforced polymer composites [14–17]. Reports of Lai et al. [15] on the thermo-mechanical properties of nanosilica reinforced poly (ether ether ketone) (PEEK) matrix at elevated temperature from 100_C to 250_ C, the effect of compactabilizers like maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted ethylene-propylene-diene copolymer (MA-EPDM) on wood-flour/polypropylene (WF/PP) composites by Chui-gen et al. [18] are some of them. The results revealed that interfacial adhesion between the PP and WF filler gets enhanced because of the presence of compactabilizers. Aravind et al. have reported the effect of compactabilization on the dynamic rheological behavior and phase morphology of PTT/ethylene propylene diene rubber (EPDM) with and without the presence of maleic anhydride grafted ethylene-propylene monomer (EPM-g-MA) [19]. In the present work, we report the improvement of modulus of PTT by decreasing the brittleness through the incorporation of MWCNT. The pure PTT and MWCNT reinforced samples were subjected to DMA to study the viscoelastic behavior and related properties like storage modulus, loss modulus, and so forth, as a function of filler loadings and temperature. Morphology of the samples was analyzed by scanning electron microscope (SEM) and transmission electron microscopy (TEM) and the changes in glass transition temperature were examined using differential scanning calorimetry (DSC). In addition, we were alwe were also able to do theoretical modelling on the viscoelastic properties of the system.

RESULTS AND DISCUSSION

Mixing of samples was done using Brabender internal mixer with a chamber volume of 55–70 cm3. Torque values which give an indication of resistance exerted by the sample on the rotor blades were measured as a function of time and also filler loading. The mixing torque value

measures the degree of homogeneity. Figure 1a shows the torque versus time of neat PTT and PTT/MWCNT nanocomposites. At the beginning of the mixing, all the samples showed higher torque value and reflects the adversity in the proper mixing of the ingredients. When mixing progresses, the torque value gradually decreases after a certain period and shows an almost smooth path with lower torque value at the end of the mixing. Lower torque value at the end indicates that the system is better mixed than in the initial mixing state. It was also observed that with increase in filler loading, the torque value also gets increased. This could be attributed to the increased melt viscosity of the nanocomposites compared to neat PTT [20]. The MWCNT was added to the melt polymer after 120 sec. A hump in the plot of torque value around 120 sec indicates an unmixed state between PTT and MWCNT. All the curves showed concentration dependent variation in the torque values. Figure 1b is the equilibrium torque versus filler loading of PTT/MWCNT nanocomposites. As expected, the equilibrium torque is seen to be increasing with increase in MWCNT content in the nanocomposites.

Given in Fig. 2 are the SEM images of the fractured surfaces of neat PTT and PTT/MWCNT nanocomposites with varying amount of MWCNT. The images show better and uniform dispersion of MWCNT in the PTT matrix when the nanofiller concentration is increased. The images also reveal the morphology of fractured surfaces. The observed results are in agreement with the data obtained from DMA analysis. SEM image of nanocomposites with 2% MWCNTshows smooth surfaces compared to other nanocomposites and neat PTT. Neat PTT and the composites containing 0.5% and 1% MWCNT show rough fracture surfaces which is evident from the brittle fracture nature of the nanocomposites. These nanocomposites with brittle nature show corresponding decrement in the storage modulus value. The agglomeration of fillers adversely affects the storage modulus value and therefore, the composite with 3 wt% MWCNT also shows a decreased storage modulus value compared to the one with 2% MWCNT content. Figure 3 shows TEM images of some of the nanocomposites. The images reveal the network formation in PTT matrix. PTT with 1% MWCNT shows some weak areas which promote reakages in the polymer matrix indicating its brittle nature which is consistent with the results obtained from its SEM image.

In DMA, sinusoidal change is applied to the samples in a cyclic manner and depending on the sinusoidal deformation, the samples show corresponding change in stiffness and damping. The applied force is sinusoidal from which we get two components, one inphase component (known as the storage modulus) which reflects the elastic behavior of material and the other out-phase component (called as the loss modulus) which corresponds to the rubbery region of the material. The damping calculated from tan delta peak is the ratio of the loss modulus and storage modulus.

The storage modulus is a direct measure of the amount of energy stored per cycle. The changes in the storage modulus with respect to change in temperature for the neat PTT and PTT/MWCNT composites are shown in Fig. 4. The plot showing temperature dependent storage modulus of PTT and the nanocomposites clearly reveal three different regions—the glassy region where the composites show high modulus, transition zone where they show decrease in the value of E0 with increase in temperature, and the rubbery region (also known as the flow region) because of the rubbery nature of the material at high temperature. Figure 4b shows that all the nanocomposites have higher storage modulus compared to pure PTT at all the temperatures studied and the value of the modulus of the composites drops significantly in the 60_C–80_C range which is in the glass transition region of the samples. The glass transition temperature (Tg) of pure composite is found to be 65.4_C. Compared to neat PTT, all the nanocomposites show increased storage modulus in both regions, the glassy as well as rubbery region. This observed behavior can be attributed to the favorable π–π interaction between the aromatic molecular contents in PTT and MWCNT. Higher storage modulus of the nanocomposites indicates that they store more energy which in turn means that they become more rigid and tough. After glass transition temperature, a sudden drop of E0 is observed which is an indication that the material becomes too soft to support the mechanical load. On increasing

temperature, the value of E0 is seen to be decreased for pure PTT and also for all the composites. This is because of the high chain mobility of the polymer which fastens their relaxation process. The E0 value for PTT/0.5% MWCNT was seen to be much higher than pure PTT at all the temperatures. This increment in E0 with the incorporation of MWCNT is essentially because of the increased interfacial adhesion and restricted mobility of the PTT chains by the addition of MWCNT [21,22]. The SEM images clearly indicate that even at smaller concentration, MWCNT get well dispersed into the PTT phase. The greater storage modulus value for PTT/MWCNT nanocomposites in the elastic region confirms the presence of highly distributed MWCNT in the PTTnanocomposites as obtained from the SEM and TEM analysis.The higher storage modulus values of nanocomposites revealed that the addition of MWCNT into the PTT matrix enhances its stiffness as well as good reinforcing capability. At 0.5 wt% loading there is an effective interaction between the polymer and MWCNT. This is evident from SEM images also. The fractured surfaces showed less brittleness. Only short linear cracks were observed for samples with lower concentrations of MWCNT. For the sample with 1 wt% MWCNT loading the SEM image (Fig. 2) showed more undulations which can be due to the brittleness of the material. The lowest storage modulus was observed for the sample with 1 wt% MWCNT. However, on loading with 2 wt% MWCNT, there was an increment in the storage modulus. At this stage, the nanofillers begin to form a network resulting in the reduction in the brittle nature. For better reinforcement, there are four main requirements—large aspect ratio, good dispersion, alignment, and stress transfer. The uniform dispersion of MWCNT with comparatively good aspect ratio is the major factor which contributes to the reinforcing properties of the nanocomposites.

The uniform dispersion of MWCNT facilitates effective and uniform stress transfer to the MWCNT network which minimizes the stress concentration centers, enhancing the properties of the system [23]. Higher storage modulus observed for the composites shows their stiffness/hardness and lesser resistance to deformation. SEM image of 2 wt% loaded nanocomposite shows less deformation compared to other nanocomposites and neat PTT. Further addition of nanofiller decreases the storage modulus value because of agglomeration of MWCNT [24–26]. From Fig. 4b, it is seen that the storage modulus value decreases for neat PTT and all other nanocomposites at higher temperatures. This is because of the increase in chain mobility of the polymers which is helpful for the relaxation process of elastic storage energy. The high storage modulus value of 2 wt% loaded composite indicates the enhanced stiffness caused by better adhesion between filler and polymer. Degree of entanglement density and reinforcement efficiency factor of the neat polymer and the nanocomposites was also calculated and the values show good agreement with the storage modulus of the various composites studied.

The π electrons in the aromatic ring of PTT interact with the CNT through π–π stacking as shown in Fig. 5. Because of the existence of π–π interaction between polymer chains and MWCNT, the nanocomposites show higher strength than neat PTT. This interaction between MWCNT and PTT will help to enhanced load transfer from the PTT to the filler and this will allow the prepared nanocomposite to withstand at higher load [27]. Due to the existence of maximum interface region, the effective stress transfer between the filler and polymer is not possible and hence the brittle nature is more predominant in the case of 1 wt% MWCNT composite as shown in Fig. 6. But at higher concentration (PTT/2% MWCNT), MWCNT form an effective network and hence the tendency for breakage is minimized. This attributed to a higher storage modulus and tensile strength of PTT/2% MWCNT nanocomposites.

From Fig. 6, it can be noticed that the intensity of tan delta peak decreased with the addition of MWCNT compared to the pure PTT composite. The peak height and sharpness of the curves showed some reduction by the addition of MWCNT because of the decrement in the chain mobility of polymers. On increasing the temperature the damping values show a maximum in the transition region, followed by a decrease in the rubbery region. Increment in filler content has reduced the tan delta values and this can be described by the reduced volume fraction by the fillers [24,30]. The magnitude of Tg of polymer depends on the mobility of polymer chains. The

polymer chain mobility is restricted which indicates that the free movement of the polymer chains is not easy and this restriction will increase the Tg. The positive shift in tan delta peak explains the reinforcing effect of MWCNT on PTT matrix.

The maximum value of tan delta peak provides the Tg of the samples. The Tg's of the nanocomposites, obtained from tan delta curves, were higher than that of pure PTT. This is because of the improved stiffness and restricted chain mobility of the polymer matrix upon MWCNT incorporation. When polymer chains are constrained by the addition of fillers the movement of the chain segments becomes hard. But at higher temperature, chain relaxation is accelerated. That is why the tan delta values reduce with temperature. Neat PTT matrix showed Tg value at 65_C and the entire nanocomposite have higher Tg than pure PTT. The composite containing 3 wt% MWCNT has got Tg value _78_C. The Tg depends on the free volume of the polymer [31].

Resalts of PTT/MWCNT nanocomposites obtained from tensile studies. This result shows same trend as that of the storage modulus obtained from DMA analysis. PTT with 2% MWCNT shows two times increment in the tensile strength compared to neat PTT as shown in Fig. 9b. The composite with 1 wt% MWCNT shows less elongation because of the higher brittleness of the composite and all the nanocomposites have achieved higher tensile modulus than neat PTT.

DSC quantifies the quantity of energy absorbed or released when a sample undergo heating or cooling. The heating and cooling curves reveal glass transition temperature (Tg), apparent melting temperature (Tm), and crystallization temperature (Tc) of the prepared samples. The DSC results are also helpful to understand the effect of MWCNT on the crystallinity of the nanocomposites. The crystallinity can be determined from DSC results using the equation % crystallinity ΔHmΔHmo on the crystallinity of the nanocomposites. The crystallinity can be determined from DSC results using the equation % crystallinityj. Cooling and (b) heating curves of nanocomposites and (c) % crystallinity versus wt% of MWCNT. obtained from the area of melting peaks, where ΔHm and ΔHmo are the heat of fusion of composite and heat of fusion of 100% crystalline PTT (146 J/g) [31]. Shows the cooling and heating curves of pure PTT and PTT/MWCNT nanocomposites obtained from dynamic DSC experiments. From the cooling curves it is clear that all the nanocomposites show higher crystallization temperature than pure PTT. This is because of the increased number of nucleus by the addition of MWCNT which enhances the crystallization temperature in nanocomposites. Among the entire nanocomposites, PTT/2% CNT shows higher crystallization temperature due to the network formation of MWCNT which restricts the polymer chain mobility. This is the reason for exhibiting high crystallization temperature by PTT/2%MWCNT nanocomposite. Due to the formation of agglomerates at higher filler loadings the chain mobility of the polymer chains are restricted. [39]. This is the reason for showing high crystallization temperature for nanocomposites having higher filler loadings. All nanocomposites show almost same melting temperature as that of the pure PTT. The Tg and Tm values obtained from DMA and DSC analysis are not same. This is because of the changes in the cooling rate of DMA and DSC analysis [40].

CONCLUSIONS

Dynamic and static mechanical properties and chain dynamics of virgin PTT and PTT/MWCNT nanocomposites are investigated. Results revealed that the incorporation of MWCNT into the PTT matrix enhances the value of the storage modulus and loss modulus and lowers tan delta value. The higher storage modulus value of nanocomposites explain its good load bearing capacity by the addition of MWCNT. The glass transition temperature of the nanocomposites also shifted to a higher temperature side by the addition of nanofiller. The reinforcement factor, degree of entanglement and PTT-MWCNT interphase adhesion factor of PTT and PTT/MWCNT nanocomposites are studied with DMA. PTT/2% CNT have showed maximum entanglement density value and reinforcement efficiency factor. PTT/2% CNT showed higher crystallization temperature and all the nanocomposites showed high Tg value than neat PTT. It is observed that the tensile properties are in close agreement with dynamic mechanical properties. The

nanocomposites prepared in the present study can be used to produce high performance engineering materials in a cost effective manner.

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